

AN X-RAY DIFFRACTION STUDY OF SOME
NORMAL LONG-CHAIN ALIPHATIC AMINE
HYDROCHLORIDES

BY

CLAUDE RAY HUDGENS

B.S., Southern Illinois Normal University, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

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INTRODUCTION

This investigation was instituted as a purely academic research with the purpose of discovering as much as possible about the crystallographic and molecular structures of the long-chain aliphatic amines. These amines are of increasing industrial importance, and as a result of this investigation, promise to be of appreciable theoretical importance. The investigation was carried as far as is possible without determining the detailed molecular structure, a task of no trivial magnitude, involving the postulation of an approximate structure by the trial-and-error method, followed by the determination of the electron density upon one or two projections of the unit cell or, as is occasionally necessary, throughout the unit cell. The determination of a detailed structure is therefore not to be undertaken lightly or without the aid of an electronic calculating machine. Fortunately, valuable, and often sufficient, information can be obtained by consideration of unit cell size, symmetry, outstanding features of the diffraction photographs, indices of refraction, chemical information, and any other type of chemical information available.

EXPERIMENTAL

The precession camera invented by Buerger was relied upon almost entirely for the determination of unit cell size and space-group symmetry. In certain cases Weissenberg and Laue photographs were used as supplemental information. Density determinations were effected by pycnometric measurement of solutions which would just suspend the crystals.

RESULTS

The compounds studied were four primary amines,

dodecyl-, tetradecyl-, hexadecyl-, and tridecylammonium chlorides, and one secondary amine, N-methyldodecylammonium chloride, prepared with considerable care and difficulty for this study by Armour & Co. With the exception of tridecylammonium chloride, these compounds crystallized in the form of platelets with the c-axis perpendicular to the face. Tridecylammonium chloride crystallized as small, distorted flakelets, also with the c-axis normal to the face. The crystallographic properties of all are summarized in the table.

TABLE OF CRYSTALLOGRAPHIC PROPERTIES

Compound	a A.	b A.	c A.	α	β	γ
$C_{12}H_{25}NH_3Cl$	5.658	7.176	17.73	90°	$92^\circ 30'$	90°
$C_{14}H_{29}NH_3Cl$	5.674	7.202	20.13	90°	$95^\circ 52'$	90°
$C_{16}H_{33}NH_3Cl$	5.708	7.242	22.56	90°	$98^\circ 21'$	90°
$C_{13}H_{27}NH_3Cl$	7.570	7.605	56.49	90°	90°	90°
$C_{12}H_{25}NH_2(CH_3)Cl$	4.978	5.287	29.92	$90^\circ 52'$	$91^\circ 52'$	$90^\circ 45'$
Compound	V A. ³	ρ_{exp}^{**}	ρ_{x-ray}	n	space-group	optic sign
$C_{12}H_{25}NH_3Cl$	719.2	1.020	1.023	2	$P2_1$	+
$C_{14}H_{29}NH_3Cl$	820.4	1.003	1.010	2	$P2_1$	—
$C_{16}H_{33}NH_3Cl$	922.9	1.005	0.9987	2	$P2_1$	—
$C_{13}H_{27}NH_3Cl$	3252	0.996	0.964	8	$C2ca$ ($Cmca$)	+
$C_{12}H_{25}NH_2(CH_3)Cl$	986.9	0.948	0.9913	2	$P\bar{1}$	—

**grams/cubic centimeter.

Dodecyl-, tetradecyl-, and hexadecylammonium chloride were all monoclinic, space-group $P2_1$. The bases of the cells of the three are almost identical in area, but show a very slight increase of the basal lengths with increasing chain length, interpreted as a decrease of the closeness of packing with increasing chain length. The length of the unit cells increase almost linearly with increase in cell length. The presence of pseudo 2_1 screw axes along the a-direction and pseudo n-glide planes normal to the c-direction place the x and y parameters

of the molecules accurately. In the case of dodecylammonium chloride, consideration of the intensities of some of the reflections have given probable values of the z -parameters, and this same information, with considerations of the diffuse reflections present in Laue photographs have established the tilt of the molecules in the unit cell as being of the order of 68° . The crystals are composed of sheets of parallel molecules, each alternate sheet turned so that a head-to-tail configuration of molecules is obtained. The crystals of this series always occurred as twins, and it is probable that they begin existence as twins.

Tridecylammonium chloride is pseudo-tetragonal orthorhombic, space-group $C2ca$ or $Cmca$. This crystal is also composed of sheets of molecules arranged in much the same way as in dodecylammonium chloride, but with molecules of the alternating sheets slightly overlapping. The pseudo symmetry and comparatively low density of this crystal indicate a high degree of molecular oscillation of the aliphatic chain around its long axis.

N-methyldodecylammonium chloride is pseudo-orthorhombic triclinic, space-group $P\bar{1}$, with unexpected similarities to tridecylammonium chloride. The general molecular configuration is a head-to-tail arrangement, but with each molecule overlapping its centrosymmetric partner by about $1/3$ of a molecular length. The molecules are in a much lower state of oscillation than tridecylammonium chloride.

OBSERVATIONS

It is significant that those crystals composed of molecules which, ignoring chemical identity, have an odd number of atoms in their chains (the even-carbon series) all crystallize in the monoclinic system, while those crystals composed of molecules whose chains have an even number of atoms crystallize in an orthorhombic or pseudo-orthorhombic system — orthorhombic if the compound is a primary amine and pseudo-orthorhombic if the compound is a secondary amine. The

implication is that chemically different but sterically similar atoms will, if placed in various positions along a chain, maintain a certain amount of isomorphism among the compounds so produced. From this study, it appears also that even-membered chains are somewhat looser packed than those containing an odd number of atoms.

The results of this study are in complete disaccord with an earlier study by J. D. Bernal.

VITA

The writer was born July 4, 1921 near Marion, Illinois. Upon graduation from the Marion high school, he entered Southern Illinois Normal University, interrupting study there in 1942 for service with the United States Army. Upon discharge from the Army in 1946, he resumed study at the same institution, graduating in 1947. He entered the Graduate School of Chemistry at the University of Illinois in June of that year, and held a half-time teaching assistantship in the Division of Analytical Chemistry from September 1947 to August 1949. During the academic year 1949-50 he held a research fellowship established by Armour & Co.

The author is a member of Sigma Xi.



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